The mechanism of fracture for entangled polymer liquids in extensional flow

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In this paper, we would like to introduce a new, improved version of a home-built filament stretcher which can reach higher controlled constant strain rates, using synchronous servomotors coupled to a tooth-belted drive axis in combination with fast feedback control of the fluid's deformation. In addition to these higher strain rates, the new filament stretcher is equipped with a rotating top plate which creates the possibility to apply a defined shear history. This feature enables the investigation of time-dependent properties by tuning the strain and shear rate history prior to extension. Several model low viscous polymer solutions are tested to validate the new set-up.

Tuesday 18:00 Marselisborg & Rosenborg PO26

Rheological behavior impact on bubbles motion in semi-dilute polymer solutions

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One of the most promising methods to improve oil production is Chemical Enhanced Oil Recovery based mainly on surfactants and polymer injection. The polymer is used to avoid digitations by increasing the water viscosity. However, a part of this additive is found back on surface and has a negative effect on water treatment. Induced gas flotation is an efficient technique to remove oil droplets from the produced water. It is mainly based on the air bubble and oil droplet attachment and combined rise. In EOR context, the hydrodynamics and interfacial phenomena are adversely affected and the flotation efficiency is reduced. To understand this impact, we first focus on the polymer influence and the consequences of its rheological properties on the bubble flow. Contrary to the dilute regime with Newtonian fluid and well dispersed bubbles, in the semi-dilute regime, the high molecular weight HPAM polymers create preferential ways for the rising bubbles and also stabilize a foam. At high concentrations, a jet of bubbles appears at the center of the column. This phenomenon is often attributed to only the solution elasticity while the HPAM solutions have a strong shear-thinning behavior. So, we propose to discuss the relative contributions of elasticity and shear-thinning to the bubble flow change. In parallel, we study the motion of successive bubbles formed with a capillary. The bubble size and speed are measured with a high-speed camera. The studies have been done with different polymer molecular weights and at high concentrations. To explain the results, rheological characterization of the HPAM solutions have been performed: shear (continuous and oscillatory) tests using a rotating rheometer and elongational rheometry within a hyperbolic microfluidic contraction. Our results highlight the impact of the polymer shear-thinning behavior on the bubble swarm motion: some bubbles are accelerated and then clusters appear. We also found a relation between the period of stress imposed by bubble passing and the relaxation time.

Tuesday 18:00 Marselisborg & Rosenborg PO27

Modeling the dynamical behavior of reinforced rubbers using a superposition approach

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The main goal of our study is to develop a superposition approach for description of the viscoelastic properties of reinforced elastomers. To investigate the influence of several factors of filler surfaces on these properties, a number of rubber compounds, based on SSBR as matrix and different types of fillers, were chosen. We used fumed silica, precipitated silica in three different grades and carbon black. The master curves were constructed with a help of a shifting procedure [1] based on the time-temperature superposition principle. To fit the master curves in the whole range of frequencies over 15 decades, we develop a superposition approach, which allows extracting the characteristics of a fully localized polymer layer on the filler surface. The complex modulus of the reinforced rubber is given as a superposition of the complex moduli of the matrix and localized layer, weighted with a volume fraction of the matrix, Cm. The frequency-dependent moduli can be described using the spectrum of relaxation times which consists of four power-low regions separated by characteristic times starting from the relaxation time of a single monomer till the terminal relaxation time [2,3]. The middle regions are characterized by the bending rigidity exponent of 3/4 and by the Rouse exponent 1/2 for the matrix. In the presence of filler the Rouse-like behaviour of the free chains changes to the slowed down behaviour of the localized chains. After successful fitting procedure we can extract the thickness of a localized layer when knowing the radius of the filler particle. In our case the layer thickness is estimated to be of the order of 5 nm. Further we can predict the filler volume fraction, at which the full localization takes place. Our results suggest that the surfaces of studied fillers impose quite different localization constraints on the rubber chains.

[1] I. Ivaneiko et al., Adv.Polym.Sci, 2017, 275, 157. [2] M. Saphiannikova et al., Macromolecules, 2014, 47, 4813. [3] I. Ivaneiko et al., Polymer, 2016, 82, 356.

Unknown ?:?? Unknown PO28

The mechanism of fracture for entangled polymer liquids in extensional flow

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In uniaxial extensional flow of entangled polymer liquids, different rupture modes may happen, including necking and fracture. Malkin and Petrie [1] proposed a "master curve" dividing the flow behavior into four zones based on the stretch rate: (I) Flow zone; (II) Transition zone; (III) Rubbery zone; and (IV) Glass-like zone. The master curve shows that steady extensional flow can only be reached in Zone I where the stretch rate is very slow, while rupture happens in Zones II-IV with faster stretch rate. Furthermore, Wang et al. [2-4] reported experimental data that matches the master curve and suggested the mechanism of rupture in Zone III and IV is disentanglement and chain scission, respectively. In this work we measure two groups of entangled polystyrene solutions. In one group the samples have the same entanglement molecular weight (Me) but different number of entanglements (Z), and in the other group the samples have the same Z but different Me. We show that in

controlled filament stretching, steady extensional flow can be reached in Zones I-III, while fracture happens in Zone IV. The critical strain at fracture decreases with increasing stretch rate, which is in agreement with the master curve in Zone IV. However, with faster rate, a constant critical strain is observed, which is not shown in the original master curve. The value of the constant critical strain seems to be related to the maximum stretch ratio of the polymer chain (determined by Me), but not influenced by Z. The results are also compared with the critical strain of chemically crosslinked polymer networks.

[1] A. Ya. Malkin and C. J. S. Petrie, J. Rheol. 41, 1-25 (1997)
[2] Y. Wang and S. Wang, Rheol. Acta. 49, 1179-1185 (2010)
[3] Y. Wang and S. Wang, Macromol. 44, 5427-5435 (2011)
[4] X. Zhu and S. Wang, J. Rheol. 57, 223-248 (2013)

Tuesday 18:00 Marselisborg & Rosenborg PO30

Varying efficiency of differential constitutive equations based on either steady shear or unsteady (LAOS) characteristics

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Efficiency of differential constitutive models (exponential Phan-Tien and Tanner, Giesekus, Leonov, and modified eXtended Pom-Pom) describing behaviour of a solution of poly(ethylene oxide) in dimethyl sulfoxide is evaluated in two steps. Firstly, nonlinear parameters of the models are optimized with the respect to steady shear measurements and consequently their ability to describe large amplitude oscillatory shear (LAOS) characteristics is tested. Secondly, nonlinear parameters of the models are optimized with the respect to LAOS measurements (both real and imaginary component of the stress amplitude are taken into account) and applicability of the models is tested against steady shear characteristics. In the first case, it is shown that the models are not capable of fitting the LAOS characteristics. In the second case, it is shown that optimization of nonlinear parameters is more responsible. Hence, a determination of the model parameters through LAOS measurements makes the models much more efficient.

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Tuesday 18:00 Marselisborg & Rosenborg PO31

Coarse-Grained Simulations for Entangled Star Polymer Melts

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In spite of the remarkable success of tube models, there still remains several issues for description of branch polymer dynamics. For example, the role of the spatial fluctuations and curvilinear hopping of the branch point have not been clarified yet. In the present work, we extend the multi-chain slip- spring (MCSS) model to focus on the dynamics of branch point. In the MCSS model, Rouse chains are temporally connected via slip-springs which mimics entanglement. The distinguishable feature of this model from the tube model is the motion of branch point. Although the branch point mobility has been examined via the multi-chain slip-link model, in the MCSS model the segmental dynamics is traced, and thus, re-equilibration process at the creation/destruction of entanglement is naturally considered. Comparison to the tube and the slip-link models will be discussed in terms of the branch point motion.

Tuesday 18:00 Marselisborg & Rosenborg PO32

On rheology of novel (co)polyesters after UV-weathering: structure/degradability relationships

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A novel class of aliphatic polyesters, and their derived copolyesters, have been developed. Beside their specific mechanical and thermal properties, the durability, in terms of biodegradability and photodurability, has been investigated. In particular, the polymers were submitted to natural and accelerated photo-ageing and an original methodology based on melt rheology has been applied to determine molecular changes upon UV weathering. Both scission and recombination reactions, which strongly compete as a function of the exposure time, were found to cause a strong evolution of the molecular structure. The results indicate that chemical structure and stereochemistry of the novel materials define the predominant process and the overall behaviour of the samples upon UV exposure. Moreover, the changes of the molecular structure, induced by UV irradiation, could have a significant role into the further biodegradability of the polymers. Therefore, while the relationships between structure and durability enable to design materials with desired well-adapted performances according to their final destination, the biodegradable character upon lifetime use is considered as really questionable and needs further studies.